Inorg. Chem. **2007**, *46*, 2846–2853

Inorganic Chemistry
Article

Biimidazole and Bis(amide)bipyridine Molybdenum Carbonyl Complexes as Anions Receptors

Laura Ion,[†] Dolores Morales,[†] Sonia Nieto,[†] Julio Pérez,[*,†] Lucía Riera,[†] Víctor Riera,[†] Daniel Miguel,[‡] Richard A. Kowenicki,[¶] and Mary McPartlin[#]

Departamento de Química Orgánica e Inorgánica—IUQOEM, Facultad de Química, Universidad de Oviedo-CSIC, 33006 Oviedo, Spain, Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain, Chemistry Department, University of Cambridge, CB2 1EW Cambridge, United Kingdom, and Department of Health and Human Sciences, London Metropolitan University, N7 8DB London, United Kingdom

Received November 14, 2006

Compounds $[Mo(CO)_4(N–N)]$ (N–N = 4,4′-bis((4-methylphenyl)carbamoyl)-2,2′-bipyridine, bipy′, **1**; or 2,2′-biimidazole, H_2biim, **2**), $[MoCl(\eta^3\text{-methallyl})(CO)_2(N–N)]$ (N–N = bipy′, **3**; H_2biim, **4**), and $[Mo(\eta^3\text{-methallyl})(CN^tBu)(CO_2)(N–N)]BAr'_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl; N–N= bipy′, **5**; H_2biim, **6**) were synthesized and characterized, and their behavior toward anions was investigated in solution (IR and ^{1}H NMR) and in solid state (X-ray diffraction).

Introduction

The incorporation of metal fragments in the structures of supramolecular anion receptors[1] can serve several purposes. In some cases, the receptor interacts with the anion through formation of a direct metal—anion bond.[2] In other instances, metal-decorated organic receptors act as chemosensors, the mission of the metal fragments being to act as reporter groups, modulating a luminescent or electrochemical signal upon interaction of the anion with some binding group.[3] Metals can provide a positive charge that adds electrostatic attraction to the noncovalent interactions at play.[4] Among these interactions, the relatively strong and directional hydrogen bonds are perhaps the most useful in receptor design. The strength of the anion···HD interactions (HD = hydrogen bond donor group) increases when a Lewis-acidic metal fragment is added to the receptor structure.[4,5] The metal can also be used as an element of geometric organization;[6] thus, ditopic molecules containing both hydrogen bond donor groups and metal-binding sites can be assembled by means of metal coordination in such a way that the several HD groups can simultaneously interact with the target anion.[7] Our group has recently applied this strategy to the design of anion receptors based on *fac*-tris(pyrazole) cationic complexes.[8] A key requisite of these complexes is their kinetic

---

[*] To whom correspondence should be addressed. E-mail: japm@uniovi.es. Fax: (34) 985103446.

[†] Universidad de Oviedo-CSIC.

[‡] Universidad de Valladolid.

[¶] University of Cambridge.

[#] London Metropolitan University.

(1) For an overview of supramolecular anion receptor chemistry, see: (a) *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., García-España, E., Eds.; Wiley-VCH: Weinheim, Germany, 1997. (b) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609. (c) Beer, P. D.; Smith, D. K. *Prog. Inorg. Chem.* **1997**, *46*, 1. (d) Antonisse, M. M. G.; Reinhoudt, D. N. *Chem. Commun.* **1998**, 443. (e) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486. (f) Gale, P. A., Ed. *Coord. Chem. Rev.* **2003**, *240*, (special issue). (g) Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671. (h) *Anion Receptor Chemistry*; Sessler, J. L., Gale, P. A., Cho, W.-S., Eds.; RSC Publishing: Cambridge, U.K., 2006. (i) Gale, P. A., Ed. *Coord. Chem. Rev.* **2006**, *250*, (special issue).

(2) (a) Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294. (b) Rudkevich, D. M.; Verboom, W.; Brzozka, Z.; Palys, M. J.; Stauthamer, W. P. R. V.; van Hummel, G. J.; Franken, S. M.; Harkema, S.; Engbersen, J. F. J.; Reinhoudt, D. M. *J. Am. Chem. Soc.* **1994**, *116*, 4341. (c) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267.

(3) For an overview of supramolecular anion sensing, see: (a) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419. (b) Anslyn, E. V., Ed. *Tetrahedron*, **2004**, *60*, (special issue).

(4) Atwood, J. L.; Holman, K. T.; Steed, J. W. *Chem. Commun.* **1996**, 1401.

(5) Camiolo, S.; Coles, S. J.; Gale, P. A.; Hurthouse, M. B.; Mayer, T. A.; Paver, M. *Chem. Commun.* **2000**, 275.

(6) Steed, J. W. *Chem. Commun.* **2006**, 2637.

(7) (a) Bondy, C. R.; Gale, P. A.; Loeb, S. J. *Chem. Commun*, **2001**, 729. (b) Bondy, C. R.; Gale, P. A.; Loeb, S. J. *J. Supramol. Chem.* **2002**, *2*, 93. (c) Bondy, C. R.; Gale, P. A.; Loeb, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 5030. (d) Wallace, K. J.; Daari, R.; Welcher, W. J.; Abouderbala, L. O.; Boutelle, M. G.; Steed, J. W. *J. Organomet. Chem.* **2003**, *666*, 63.

(8) (a) Nieto, S.; Pérez, J.; Riera, V.; Miguel, D.; Alvarez, C. *Chem. Commun.* **2005**, 546. (b) Nieto, S.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Chem.—Eur. J.* **2006**, *12*, 2244.

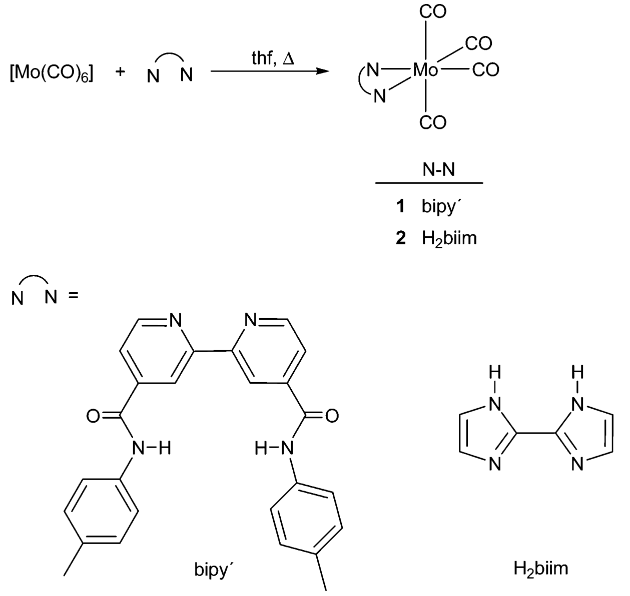
10.1021/ic0621650 CCC: $37.00

substitutional inertness, without which simple substitution of the neutral ligands by the target anion would occur.[7b,d] Last, and the most pertinent to the work that we wish to report here, metal coordination of a bis(ditopic) molecule such as 2,2′-biimidazole (H_2biim) (a) enforces the *syn* conformation of H_2biim, the optimal one for simultaneous interaction of anions with both biimidazole N−H groups and (b) precludes H_2biim self-association, which would otherwise result in a reduced solubility and compete against anion binding. We have previously illustrated these features using the cationic complex $[RuCl(\eta^6\text{-}p\text{-cymene})(H_2biim)]^+$, prepared as its $BAr'_4{}^-$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl) salt in order to avoid competition of the counteranion with the target, external anion and to enhance solubility in organic, moderately polar solvents.[9] Unlike the complexes of the monodentate pyrazole ligands mentioned previously in this Article, metal complexes of bidentate ligands such as H_2biim can be expected to be, as a result of the chelate effect, kinetically robust against dissociation for a wide range of metal fragments. Therefore, employment of third-row metals such as rhenium or platinum should not be necessary. For the present study, we have chosen molybdenum carbonyl fragments because, as it will be shown in what follows, their complexes with the chelating, N-donor ligands are easily accessible in two different metal oxidation states, and both neutral and cationic complexes (we have previously developed methods to prepare the latter as their $BAr'_4{}^-$ salts)[10] can be prepared. That presents us with the opportunity of comparing the behavior toward anions of complexes featuring the same metal and bidentate ditopic ligand but with different charge and metal oxidation state. $\{Mo(CO)_4\}$ and $\{Mo(\eta^3\text{-allyl})(CO)_2\}$ complexes of bidentate, N-donor heterocyclic ligands are quite air and moisture stable. In addition, the integrity of the complexes in the presence of external anions can be readily ascertained by observing the strong ν(CO) bands, occurring in a clean region of the IR spectrum. As the bis(ditopic) bidentate ligands, we have chosen, in addition to H_2biim, an example of a 4,4′-bis(carbamoyl)-2,2′-bipyridine, a type of ligand in which, as in 2,2′-biimidazole itself, metal coordination impedes rotation around the central C−C bond, imposing the conformation best suited for the interaction with anions, and whose rhenium(I) and ruthenium(II) complexes have been extensively studied by the group of Beer in the context of supramolecular anion binding and sensing.[11]

Results and Discussion

Neutral molybdenum(0) *cis*-tetracarbonyl complexes $[Mo(CO)_4(N{-}N)]$ (N−N = 4,4′-bis((4-methylphenyl)carbamoyl)-2,2′-bipyridine, bipy′, **1**; or 2,2′-biimidazole, H_2biim, **2**, a previously known complex)[12] were prepared by the reaction of $Mo(CO)_6$ with an equimolar amount of the respective ligand in refluxing tetrahydrofuran (thf), as described in the Experimental Section and shown in Scheme 1.[10]

Scheme 1. Synthesis of Molybdenum(0) Complexes **1** and **2**



Both compounds were found to be virtually insoluble in toluene, dichloromethane, acetone, thf, and acetonitrile, a fact that can be attributed to intermolecular hydrogen bonding between the biimidazole or amide N−H groups and the oxygens of carbonyl ligands. Thus, intermolecular hydrogen bonding involving N−H groups and carbonyl ligands has been demonstrated for the very insoluble complex *cis*-$[Mo(CO)_4(Hdmpz)_2]$ (Hdmpz = 3,5-dimethylpyrazole) by Villafañe et al.[13−14]

Compound $[Mo(bipy')(CO)_4]$ (**1**) was found to be soluble enough in DMSO-d_6, and the effect of the addition of several anions (as tetrabutylammonium salts) was studied by ^1H NMR. Significant shifts to higher frequencies were observed for the signals corresponding to the hydrogens of the amide N−H groups as well as for the hydrogens of the 3,3′ carbons of the bipyridine upon addition of chloride, dihydrogenphosphate, and acetate, whereas for bromide, iodide, nitrate, or hydrogensulfate, the variation was imperceptible. The persistence of a *cis*-$Mo(CO)_4$ IR pattern indicated the stability

---

[9] Ion, L.; Morales, D.; Pérez, J.; Riera, L.; Riera, V.; Kowenicki, R. A.; McPartlin, M. *Chem. Commun*. **2006**, 91.

[10] Pérez, J.; Morales, D.; Nieto, S.; Riera, L.; Riera, V.; Miguel, D. *Dalton Trans*. **2005**, 884.

[11] (a) Beer, P. D.; Dickson, C. A. P.; Fletcher, N.; Goulden, A. J.; Grieve, A.; Hodacova, J.; Wear, T. *J. Chem. Soc., Chem. Commun*. **1993**, 828. (b) Beer, P. D.; Dent, S. W.; Hobbs, G. S.; Wear, T. J. *Chem. Commun*. **1997**, 9. (c) Szemes, F.; Hesek, D.; Chen, Z.; Dent, S. W.; Drew, M. G. B.; Goulden, A. J.; Graydon, A. R.; Grieve, A.; Mortimer, R. J.; Wear, T.; Weightman, J. S.; Beer, P. D. *Inorg. Chem*. **1996**, *35*, 5868. (d) Beer, P. D.; Szemes, F.; Balzani, V.; Salà, C. M.; Drew, M. G. B.; Dent, S. W.; Maestri, M. *J. Am. Chem. Soc*. **1997**, *119*, 11864. (e) Cooper, J. B.; Drew, M. G. B.; Beer, P. D. *Dalton Trans*. **2001**, 39. (f) Uppadine, L. H.; Keene, F. R.; Beer, P. D. *Dalton Trans*. **2001**, 218. (g) Uppadine, L. H.; Redman, J. E.; Dent, S. W.; Drew, M. G. B.; Beer, P. D. *Inorg. Chem*. **2001**, *40*, 2860; (h) Uppadine, L. H.; Drew, M. G. B.; Beer, P. D. *Chem. Commun*. **2001**, 29. (i) Vickers, M. S.; Martindale, K. S.; Beer, P. D. *J. Mater. Chem*. **2005**, *15*, 2784.

[12] Beck, W.; Goetzfried, F.; Riederer, M. *Z. Anorg. Allg. Chem*. **1976**, *423*, 97.

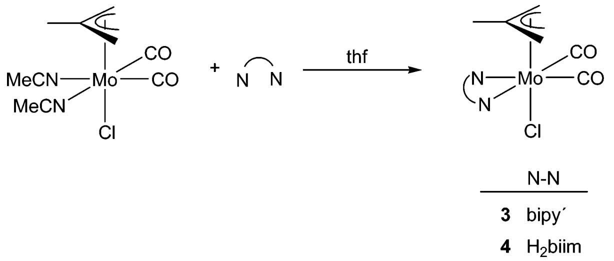
[13] For a precedent of the employment of the molybdenum tetracarbonyl fragment in the construction of anion receptors, see: Kingston, J. E.; Ashford, L.; Beer, P. D.; Drew, M. G. B. *Dalton Trans*. **1999**, 251.

[14] Paredes, P.; Arroyo, M.; Miguel, D.; Villafañe, F. *J. Organomet. Chem*. **2003**, *667*, 120. For additional examples of carbonyl ligands as hydrogen bond acceptors, see: ref 5 and (a) Braga, D.; Grepioni, F. *Acc. Chem. Res*. **1997**, *30*, 81. (b) Haiduc, I.; Edelmann, F. T. *Supramolecular Organometallic Chemistry*;Wiley-VCH: Weinheim, Germany, 1999, p 352

Table 1. Binding Constant Values for Compound **1** in DMSO-d_6

anion	K_a (M^{-1})
Cl^-	662 ± 1
$H_2PO_4^-$	856 ± 50
OAc^-	397 ± 29

Scheme 2. Synthesis of Neutral Molybdenum(II) Compounds **3** and **4**



of **1** toward these anions, and anion exchange was found to be fast. The results of ^1H NMR titrations were used to calculate the 1:1 binding constants (Table 1). The very low solubility of compound [$Mo(CO)_4(H_2biim)$] (**2**) even in the more polar dimethylsulfoxide precluded the NMR study of its solution behavior toward anions.

Neutral molybdenum(II) *cis*-dicarbonyl complexes [MoCl(η^3-methallyl)(bipy′)$(CO)_2$] (**3**) and [MoCl(η^3-methallyl)-$(CO)_2(H_2biim)$] (**4**) were prepared by reaction of the respective bidentate ligand with the labile precursor [MoCl(η^3-methallyl)$(CO)_2(NCMe)_2$][10] (see Experimental Section and Scheme 2). The IR spectra were found to feature pairs of ν(CO) bands of similar intensity at 1942 and 1871 (**3**) and 1947 and 1852 (**4**) cm^{-1}, values similar to those found for previously characterized *cis*-dicarbonyl [MoX(η^3-allyl)$(CO)_2$-(N−N)] complexes.[15]

Complexes **3** and **4** showed a very low solubility in organic solvents. The extremely insoluble complex [MoCl(η^3-allyl)$(CO)_2(H_2biim)$], closely similar to **4**, was previously reported by Calhorda et al.[16] The low solubility of this type of complexes can be attributed to intermolecular hydrogen bonding between the N−H groups and the Cl ligand, the best hydrogen bond acceptor in these complexes. A closely related topic, namely, the hydrogen bonds between halide ligands and urea, has been recently studied by Steed et al.[17] Due to the low solubility of **3** and **4** in most solvents, DMSO-d_6 had to be used again for the NMR studies. Fast anion exchange was found, and the calculated binding constants are listed in Table 2. For the bipy′ complex **3**, again only the chloride, dihydrogenphosphate, and acetate anions gave rise to visible changes in the ^1H NMR spectrum.

The Bu_4N salt of the **3**·[Cl^-] adduct could be isolated by crystallization, and its solid-state structure was determined by means of single-crystal X-ray diffraction. The structure of the **3**·[Cl^-] adduct is displayed in Figure 1.

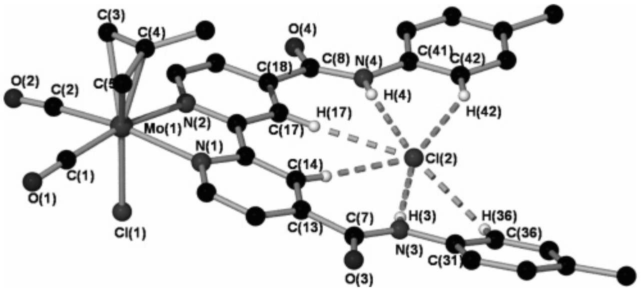


Figure 1. Molecular structure of the [MoCl(η^3-methallyl)(bipy′)$(CO)_2$]·[Cl^-] adduct.

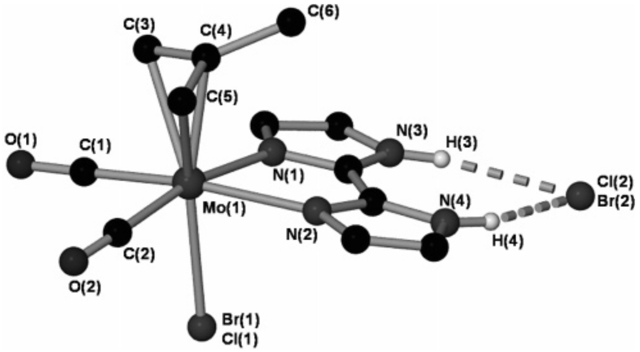


Figure 2. Molecular structure of the [Mo(Cl/Br)(η^3-methallyl)$(CO)_2(H_2biim)$]·[Cl/Br^-] adduct.

Table 2. Binding Constant Values for Compounds **3** and **4** in DMSO-d_6

anion	**3**, K_a (M^{-1})	**4**, K_a (M^{-1})
Cl^-	571 ± 0.6	196 ± 7
Br^-		927 ± 30
$H_2PO_4^-$	257 ± 16	
OAc^-	342 ± 30	

The structure confirms the presence of the [MoCl(η^3-methallyl)(bipy′)$(CO)_2$]·[Cl^-] supramolecular adduct, and the hydrogen-bonding pattern is similar to those previously found by Beer and co-workers for metal complexes of 4,4′-bis-(arylcarbamoyl)-2,2′-bipyridine ligands;[11c] the non-metal-coordinated chloride interacts with the two amide N−H hydrogens (N(3)···Cl(2) = 3.363(6) and N(4)···Cl(2) = 3.351(7) Å; N(3)−H(3)···Cl(2) = 165(6) and N(4)−H(4)···Cl(2) = 169(7)°), the two hydrogens at the C_3 and $C_{3'}$ carbons of the bipyridine framework (C(14)···Cl(2) = 3.512(7) and C(17)···Cl(2) = 3.497(7) Å; C(14)−H···Cl(2) = 173.1(1) and C(17)−H···Cl(2) = 176.2(1)°), and two of the *ortho*-C−H groups of the aryl substituents (C(36)···Cl(2) = 3.554(7) and C(42)···Cl(2) = 3.613(8) Å; C(36)−H···Cl(2) = 140.6(1) and C(42)−H···Cl(2)= 147.7(1)°).

For complex [MoCl(η^3-methallyl)$(CO)_2(H_2biim)$] (**4**), significant ^1H NMR downfield shifts were seen upon addition of chloride and also of bromide. The relative magnitude of the binding constants for these anions, calculated from ^1H NMR titrations (see Table 2), was somewhat unexpected (higher for bromide), and the determination of the solid-state structure of the bromide adduct was sought. The addition of the equimolar amount of tetrabutylammonium bromide onto a saturated thf solution of **4**, followed by the slow (2 days) diffusion of hexane, afforded yellow, X-ray quality crystals, one of which was used for the structural determination. The results indicated a [Bu_4N][MoX(η^3-methallyl)$(CO)_2(H_2biim)$]·[Y] composition (see Figure 2),

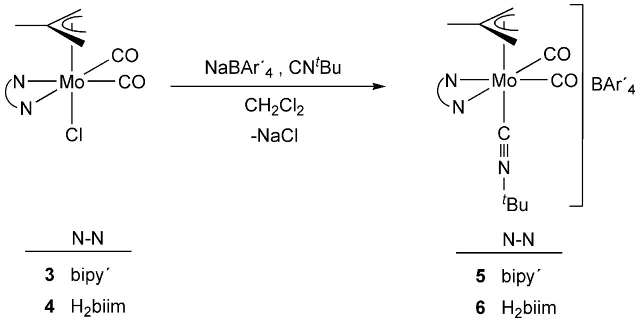
---

(15) tom Dieck, H.; Friedel, H. *J. Organomet. Chem.* **1968**, *14*, 375.

(16) Pinto, P.; Barranco, E.; Calhorda, M. J.; Félix, V.; Drew, M. G. *J. Organomet. Chem.* **2000**, *601*, 34.

(17) Turner, D. R.; Smith, B.; Goeta, A. E.; Evans, I. R.; Tocher, D. A.; Howard, J. A. K.; Steed, J. W. *CrystEngComm* **2004**, *6*, 633.

Scheme 3. Synthesis of Cationic Molybdenum(II) Complexes **5** and **6**



where the chloride and bromide anions are approximately 50% disordered between the X and Y positions.

This demonstrates that the chloride ligand in **4** undergoes substitution by external anions; at least, it partly does by bromide over a 2 day period. Taking into account that the IR and ^{1}H NMR spectra of [MoX(η^3-allyl)(CO)$_2$(N−N)] (X = Cl, Br) complexes are similar, we note that the stability of such complexes toward external anions cannot be easily ascertained by spectroscopic means. In such a situation, the binding constants for **3** and **4** (Table 2) cannot be relied upon. The fact that a halide ligand is labile in complexes of the type [MoX(η^3-allyl)(CO)$_2$(N−N)] is not surprising; in fact, in previous works (also, see later in this Article), we have prepared [Mo(η^3-allyl)(CO)$_2$(N−N)L]BAr′$_4$ (L = neutral monodentate ligand) compounds by reaction of the corresponding [MoCl(η^3-allyl)(CO)$_2$(N−N)] precursor with L and the NaBAr′$_4$ salt (note that sodium salts are not strong halide-abstracting reagents).[18] A similar halide metathesis during an attempt to crystallize a supramolecular adduct containing a rhenium tricarbonyl bipyridine fragment was reported by Beer et al.,[11g] and halide substitution occurs less readily in rhenium tricarbonyl complexes than it does in [MoX(η^3-allyl)(CO)$_2$(N−N)].

In view of the results described, we set out to replace the chloride in complexes **3** and **4** by other ligands such that the products are spectroscopically very different from the neutral [MoX(η^3-methallyl)(CO)$_2$(N−N)] complexes, the potential anation products, thus allowing for a conclusive diagnostic of the stability of the molybdenum complexes. The reactions of **3** or **4** with the equimolar amounts of *tert*-butylisocyanide and NaBAr′$_4$ afforded, as single products, the new compounds [Mo(η^3-methallyl)(CN^{t}Bu)(CO)$_2$(N−N)]-BAr′$_4$ (N−N = bipy′, **5**; H$_2$biim, **6**), which were isolated as crystalline solids, as detailed in the Experimental Section (see Scheme 3). The shift to higher frequencies (compared with those of the neutral precursors **3** and **4**) in the IR ν(CO) bands (at 1965 and 1894 cm^{-1} for **5** and at 1961 and 1881 cm^{-1} for **6**) was consistent with the formation of cationic compounds. Compounds **5** and **6** were characterized by IR and NMR spectroscopy (see Experimental Section).[19]

Table 3. Binding Constant Values for Compounds **5** and **6** in CD$_3$CN

anion	**5**, K_a (M^{-1})	**6**, K_a (M^{-1})
Cl$^-$	17169 ± 1141	11452 ± 1152
Br$^-$	7183 ± 277	10496 ± 681
I$^-$	217 ± 17	315 ± 51
NO$_3^-$	992 ± 15	10693 ± 939
HSO$_4^-$	779 ± 11	10447 ± 781
OAc$^-$	342 ± 30	
ReO$_4^-$	25 ± 91	436 ± 47

The IR spectroscopy provided a quick, unambiguous way to assess if an external anion displaces the monodentate CN^{t}Bu ligand. Thus, such a substitution would transform a cationic complex into a neutral one, significantly shifting the ν(CO) bands to lower wavenumber values (see previous paragraphs). Moreover, the medium-intensity isocyanide ν(CN) band would shift from 2185 to 2140 cm^{-1} (free CN^{t}Bu) upon substitution of the isocyanide ligand.

Compounds [Mo(η^3-methallyl)(CN^{t}Bu)(bipy′)(CO)$_2$]BAr′$_4$ (**5**) and [Mo(η^3-methallyl)(CN^{t}Bu)(CO)$_2$(H$_2$biim)]BAr′$_4$ (**6**) were found to be highly soluble in dichloromethane, thf, and acetonitrile. The fact, surprising at first sight, that these salts are much more soluble in moderately polar organic solvents than the neutral complexes **1**−**4** discussed in the preceding sections can be attributed to the large delocalization of the negative charge over the large BAr′$_4^-$ anion, the lack of good hydrogen bond acceptor groups on this anion, and the fact that the extent of inter-cation hydrogen bonding (e.g., between N−H groups and CO ligands, as those mentioned for the neutral tetracarbonyls) would now be opposed by Coulombic repulsion and by anion interposition. It is pertinent to note here that the compound [RuCl(η^6-*p*-cymene)(H$_2$biim)]BAr′$_4$,[9] containing the good hydrogen bond acceptor chloride, has been also found to be very soluble in dichloromethane, thf, and acetonitrile.

The behavior of compounds **5** and **6** toward several anions in solution was investigated spectroscopically. IR and ^{1}H NMR showed that **5** and **6** are stable (i.e.; they do not undergo substitution of the monodentate CN^{t}Bu ligand) in the presence of several anions (see the following discussion). The addition of Bu$_4$NX salts to solutions of **5** or **6** in CD$_3$CN led to large downfield shifts in the ^{1}H NMR signals of the amide **5** or biimidazole **6** N−H groups, indicating strong hydrogen bonding. The IR ν(CO) bands of **5** and **6** underwent relatively small shifts to lower frequencies upon anion addition (for instance, only 5 (**5**) or 7 cm^{-1} (**6**) for the chloride anion, in contrast with the much larger difference between the neutral Mo−Cl and cationic Mo−CN^{t}Bu complexes), which is attributed to the electron density release from the anion to the hydrogen bond acceptor groups and, from these, through the ligand framework to the metal centers.[20]

Anion exchange was found to be fast, and 1:1 binding constants (Job plots are shown in Figure 3 (**6**) and in the

---

[18] Morales, D.; Navarro Clemente, M. E.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Organometallics* **2002**, *21*, 4934.

[19] For previous works in Mo allylisocyanide chemistry, see: (a) King, R. B.; Saran, M. S. *Inorg. Chem.* **1974**, *13*, 2453. (b) Deaton, J. C.; Walton, R. A. *J. Organomet. Chem.* **1981**, *219*, 187. To the best of our knowledge, no examples of pseudooctahedral cationic allyl molybdenum isocyanide complexes have been previously reported.

[20] For a previous application of IR spectroscopy in the ν(CO) region to the study of hydrogen bonding in solution, see: Peris, E.; Mata, J. A.; Moliner, V. *J. Chem. Soc,. Dalton Trans.* **1999**, 3893. For an application of IR spectroscopy in the ν(CO) region to the solution behavior of a cation receptor, see: Anson, C. E.; Creaser, C. S.; Stephenson, G. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2175.

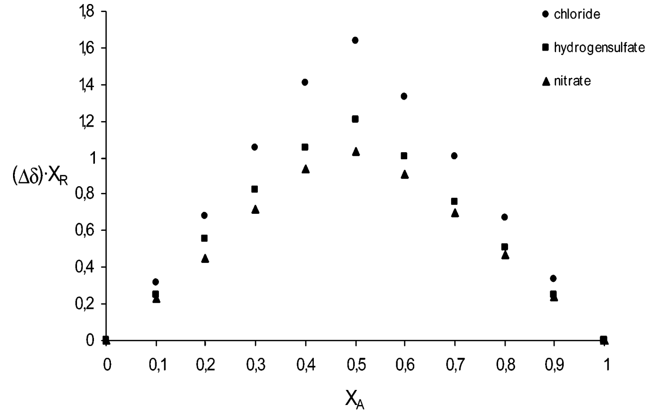


Figure 3. Job plot of receptor **6** toward chloride, hydrogensulfate, and nitrate anions.

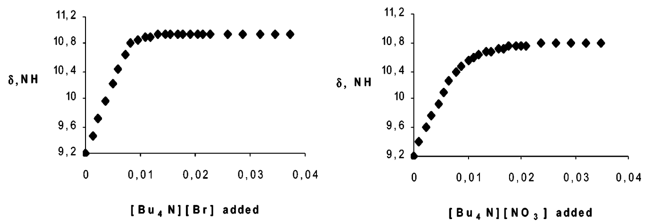


Figure 4. ^{1}H NMR titration plots of receptor **5** with bromide and nitrate anions in CD_3CN.

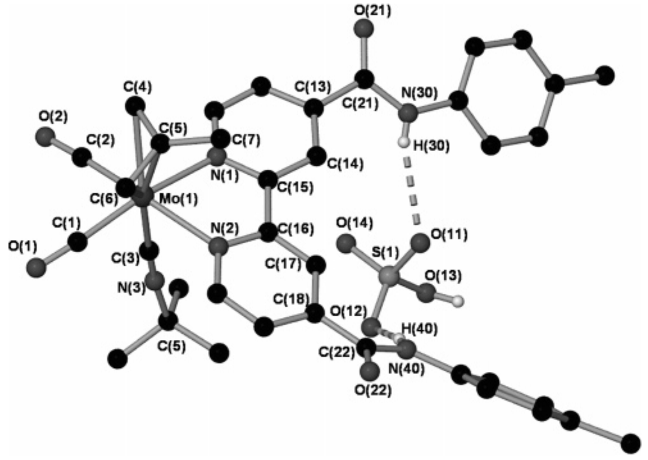


Figure 5. Molecular structure of the [Mo(η^3-methallyl)(CN^{t}Bu)(bipy′)-$(CO)_2$]·[HSO_4] adduct.

Supporting Information (**5**)) were obtained from ^{1}H NMR titrations in CD_3CN (see Figure 4, Table 3, and Supporting Information), a solvent less competitive than DMSO and in which significant downfield shifts in the ^{1}H NMR signals could be observed for several anions.

Attempts to obtain X-ray quality crystals from solutions containing equimolar mixtures of either **5** or **6** and Bu_4NX salts were successful for **5** and hydrogensulfate and for **6** and bromide and perrhenate anions. The results of the structural determinations (Figures 5 and 6) indicate the formation of neutral supramolecular 1:1 adducts of the composition [Mo(η^3-methallyl)(CN^{t}Bu)$(CO)_2$(N−N)]·[X], which crystallize separately from the salt [Bu_4N][BAr′$_4$], a fact previously found by us.[8b,9]

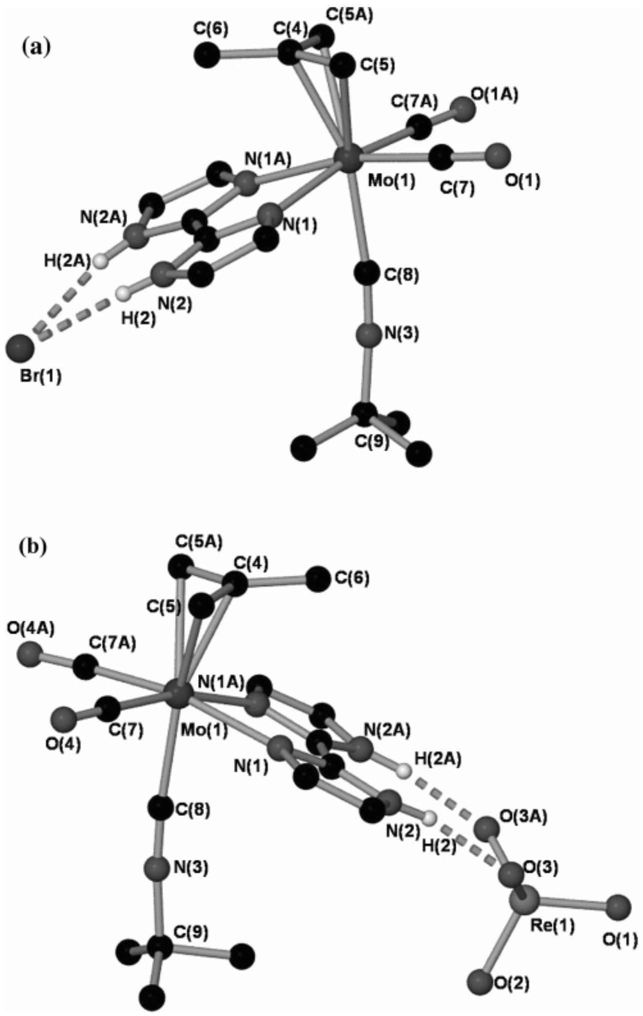


Figure 6. (a) Molecular structure of the [Mo(η^3-methallyl)(CN^{t}Bu)(H_2-biim)$(CO)_2$]·[Br] adduct; (b) molecular structure of the [Mo(η^3-methallyl)(CN^t-Bu)(H_2biim)$(CO)_2$]·[ReO_4] adduct.

A common feature of the solid-state structures of the adducts of **5** and **6** is their C_2 symmetry. The geometry around molybdenum can be described as pseudooctahedral, with an equatorial plane defined by the two nitrogen donor atoms of the bipy′ or H_2biim chelate and the two carbonyls and the isocyanide and η^3-methallyl ligands occupying mutually *trans* positions. The Mo−CNBu^t distances, in the 2.1−2.2 Å range, while longer than those found for the Mo−CO bonds (1.9−2.0 Å), are comparable with Mo−CN[21] or Mo−C(alkynyl)[22] distances found in neutral complexes [Mo(η^3-allyl)X$(CO)_2$(N−N)] (X = cyanide or alkynyl; N−N = 2,2-bipyridine or 1,10-phenanthroline) with similar geometries. This suggests strong Mo−isocyanide bonds, in accordance with the stability of the cationic complexes even in the presence of anions.

In the **5**·HSO_4 adduct, each of the amide N−H groups forms a hydrogen bond to one of the HSO_4 oxygen atoms. One of these two oxygen atoms, O(12), is so much out of the bipy′ plane that the formation of its hydrogen bond to the N(40)−H group forces the *p*-tolylcarbamoyl moiety out

---

(21) Hevia, E.; Pérez, J.; Riera, L.; Riera, V.; García-Granda, S.; García-Rodríguez, E.; Miguel, D. *Eur. J. Inorg. Chem.* **2003**, 1113.

(22) (a) Pérez, J.; Riera, L.; Riera, V.; García-Granda, S.; García-Rodríguez, E.; Miguel, D. *Chem. Commun.* **2002**, 384. (b) Pérez, J.; Riera, L.; Riera, V.; García-Granda, S.; García-Rodríguez, E.; Miguel, *Organometallics* **2002**, *21*, 1622.

Table 4. Crystal Data and Refinement Details

	3·[Bu_4NCl]	**[Mo(Cl/Br)(η^3-methallyl)(bipy′)($CO)_2$]·[Cl/Br^-]**	**5·[HSO_4]**	**6·[Br]**	**6·[ReO_4]**
formula	$C_{48}H_{60}Cl_2MoN_5O_4$	$C_{28.25}H_{49.50}BrCl_{1.50}MoN_5O_2$	$C_{37}H_{39}MoN_5O_8S$	$C_{17}H_{22}BrMoN_5O_2$	$C_{17}H_{22}MoN_5O_6Re$
M_r	937.85	720.25	809.73	504.25	674.54
cryst syst	orthorhombic	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	$P2(1)2(1)2(1)$	$Fdd2$	$P2(1)/c$	$Ibam$	$Pnma$
a [Å]	14.431(17)	37.006(5)	9.179(2)	29.195(6)	16.411(3)
b [Å]	15.904(19)	39.403(5)	26.858(6)	12.039(2)	10.172(2)
c [Å]	21.68(3)	10.1814(14)	16.629(4)	12.783(3)	14.171(3)
α [°]	90	90	90	90	90
β [°]	90	90	102.285(4)	90	90
γ [°]	90	90	90	90	90
V [$Å^3$]	4975(10)	14846(4)	4005.7(15)	4492.5(16)	2365.6(8)
Z	4	16	4	8	4
T_c [K]	293(2)	296(2)	293(2)	180(2)	180(2)
ρ_{calcd} [g cm^{-3}]	1.252	1.289	1.343	1.491	1.894
$F(000)$	1964	1567	1672	2016	1296
λ(Mo Kα) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
cryst size [mm]	0.19 × 0.32 × 0.48	0.13 × 0.12 × 0.12	0.23 × 0.16 × 0.04	0.23 × 0.14 × 0.01	0.14 × 0.10 × 0.02
μ[mm^{-1}]	0.416	1.567	0.433	2.381	5.682
scan range [°]	$1.74 \leq \theta \leq 23.24$	$1.51 \leq \theta \leq 23.29$	$1.46 \leq \theta \leq 23.31$	$3.63 \leq \theta \leq 27.46$	$3.72 \leq \theta \leq 25.06$
refl. measured	21813	16736	18150	15537	13710
independent refl.	7067	4552	5771	2687	2206
data/ restraints/ parameters	7067/0/554	4552/1/356	5771/0/482	2687/0/150	2206/1/162
goodness-of-fit on F^2	1.076	1.033	1.025	1.105	1.142
R_1/R_{w2} [$I > 2\sigma(I)$]	0.0497/ 0.1067	0.0602/ 0.1443	0.0452/ 0.0787	0.0490/ 0.0944	0.0502/ 0.0966
R_1/R_{w2} (all data)	0.0755/ 0.1245	0.1163/ 0.1582	0.0935/ 0.0858	0.0680/ 0.1011	0.0797/ 0.1067

of the same plane (see Figure 5). While the adoption of such a geometry allows the formation of the two simultaneous hydrogen bonds (N(30)···O(11) = 3.185(6) Å, N(30)···H···O(11) = 161.5(6)°; N(40)···O(12) = 3.011(5) Å, N(40)···H···O(12) = 167.4(5)°), it also involves an unfavorable loss of conjugation, which should partially account for the relatively low value of the binding constant calculated for receptor **5** and the hydrogensulfate anion. The magnitude of the effect can be realized by comparing (see Table 3) the large differences between the binding constants for this anion and those for either the chloride or bromide for receptor **5** with the same differences, which are much smaller, found for receptor **6**. The geometry of the **6**−hydrogensulfate adduct could not be crystallographically demonstrated; in the absence of such evidence, the most favorable arrangement most likely involves the same nine-membered ring, as described in the following for the adduct formed between **6** and the tetrahedral perrhenate anion; the high values of the binding constants found for **6** and hydrogensulfate or nitrate anions suggest the formation of this particularly favorable ring structure.

The bromide anion in the **6**·[Br] adduct forms two strong hydrogen bonds with the two biimidazole N−H groups (N···Br = 3.289(4) Å, N···H···Br = 164(5)°),[11d] in line with the relatively high binding constant. In the **6**·[ReO_4] adduct, each of the biimidazole N−H groups forms a hydrogen bond to one of the perrhenate oxygens (N···O = 2.76(1) Å, N···H···O = 165.4°), forming a nine-membered ring as the one previously found by us for the nitrate anion and a ruthenium biimidazole complex.[9]

The most interesting difference between receptors **5** and **6** in their behavior toward anions is that binding constants were found to span a wide range of values for the former. This fact can be attributed to the more discriminating nature of the cavity, comprising up to six hydrogen bond donor groups (two N−H and four C−H groups, see the structure of the [MoCl(η^3-methallyl)(bipy′)($CO)_2$]·[Cl^-] adduct), created by the backside of the bipy′ ligand. The fact that such a discrimination is effected by the cationic receptor of **5** is noteworthy since one of the drawbacks of cationic receptors for anions is that the Coulombic attraction tends to make them fairly unselective. On the other hand, the relatively large values of some of the binding constants encountered for **5** and **6** and the fact that the interaction in CD_3CN solution can be detected (and measured) even for the large, charge-delocalized anions such as iodide or perrhenate can be, at least in part, attributed to the choice of the low interacting $BAr'_4{}^-$ counteranion.

Conclusion

The neutral complexes [Mo($CO)_4$(N−N)] (**1**, **2**) and [MoCl(η^3-methallyl)($CO)_2$(N−N)] (**3**, **4**) are very insoluble, a fact attributed to intermolecular hydrogen bonding. The stability of **3** and **4** toward external anions could not be unambiguously demonstrated by spectroscopic means, and at least in one case, partial chloride substitution was found. In contrast, compounds [Mo(η^3-methallyl)($CNBu^t$)($CO)_2$(N−N)]BAr'_4 (**5**, **6**) display a high solubility in moderately polar organic solvents and are stable in solution toward external anions, as it can be easily ascertained by IR spectroscopy. ^1H NMR studies of the behavior of **5** and **6** toward several anions indicated fast anion exchange, formation of 1:1 supramolecular adducts, and binding constants spanning a broad range. The variation of the magnitude of the binding constants with the nature of the anion is higher for **5**, the bis(amide)bipyridine ligand, which is able to establish up to six hydrogen bonds with a chloride anion, as demonstrated by X-ray crystallography.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using Schlenk techniques. Compound **2** was prepared as previously reported.[12] Tetrabutylammonium salts were purchased from Fluka or Aldrich. Deuterated acetonitrile and dimethylsulfoxide (Cambridge Isotope Laboratories, Inc.) were stored under nitrogen in Young tubes and used without further purification. NMR spectra were recorded on Bruker AC-300 and DPX-300 instruments. IR solution spectra were obtained by a Perkin-Elmer FT 1720-X spectrometer using 0.2 mm CaF_2 cells. NMR samples were prepared under nitrogen using Kontes manifolds purchased from Aldrich. Oven-dried, 5 mm NMR tubes were subjected to several vacuum−nitrogen cycles, filled with the solution of the receptor (prepared separately in a Schlenk tube, typically in a 10^{-2} M concentration in CD_3CN) by means of a 1 mL syringe, and stoppered with rubber septa. After the H^1 NMR spectrum of the receptor was recorded, the successive aliquots of the tetrabutylammonium salt (typically 4×10^{-2} M in CD_3CN, separately prepared and kept in a septum-stoppered vial during the titration) were injected through the septum using Hamilton microsyringes (10−100 μL). The volume of each addition was 10 μL before reaching the saturation zone (nearly horizontal line of the titration profile), and was 20 or 40 μL afterward. When the change in δ is small (as for ReO_4^-), 20 μL of salt solution was added from the beginning. Data were treated using the WinEQNMR program.[23]

Synthesis of [Mo(bipy′)(CO)$_4$] (1). A mixture of $[Mo(CO)_6]$ (0.150 g, 0.568 mmol) and bipy′ (0.240 g, 0.568 mmol) in thf (40 mL) was refluxed for 4 h. The solution was concentrated under vacuum to a volume of 5 mL, and addition of diethylether (20 mL) caused the precipitation of compound **1** as a red, microcrystalline solid, which was washed with hexane (2 × 20 mL). Yield: 0.250 g, 70%. IR (thf, cm^{-1}): 2012, 1906, 1888, 1846 (ν_{CO}). ^1H NMR (DMSO-d_6): δ 10.79 (br s, 2H, NH, bipy′), 9.32 (s, 2H, bipy′), 9.04 (d, J(H,H) = 5.2 Hz, 2H, bipy′), 8.11 (d, J(H,H) = 5.2 Hz, 2H, bipy′), 7.70, 7.67, 7.24, 7.22 (AA′BB′, 8H, C_6H_4 of bipy′), 2.43 (s, 6H, CH_3, bipy′). ^{13}C NMR (DMSO-d_6): δ 222.0 (2 × CO), 204.6 (2 × CO), 163.6 (C=O, bipy′), 155.3, 150.0, 143.4, 136.0, 133.2, 121.6, 120.5, 129.0, 118.4 (bipy′), 20.4 (CH_3, bipy′). Anal. Calcd (%) for $C_{30}H_{22}MoN_4O_6$: C, 57.15; H, 3.52; N, 8.84. Found: C, 57.33; H, 3.48; N, 8.77.

Synthesis of [MoCl(η^3-methallyl)(bipy′)(CO)$_2$] (3). A mixture of [MoCl(η^3-methallyl)$(CO)_2(NCMe)_2$] (0.050 g, 0.153 mmol) and bipy′ (0.065 g, 0.153 mmol) in thf (20 mL) was stirred at room temperature for 30 min. The resulting dark solution was concentrated under vacuum to a volume of 5 mL, and addition of diethylether (20 mL) caused the precipitation of compound **3** as a microcrystalline solid, which was washed with hexane (2 × 20 mL). Yield: 0.096 g, 94%. IR (thf, cm^{-1}): 1942, 1871 (ν_{CO}). ^1H NMR (DMSO-d_6): δ 10.73 (br s, 2H, NH, bipy′), 9.12 (s, 2H, bipy′), 8.97 (d, J(H,H) = 5.2 Hz, 2H, bipy′), 8.07 (d, J(H,H) = 5.2 Hz, 2H, bipy′), 7.67, 7.65, 7.22, 7.19 (AA′BB′, 8H, C_6H_4 of bipy′), 2.93 (s, 2H, H_{syn} methallyl), 2.31 (s, 6H, CH_3, bipy′), 1.35 (s, 2H, H_{anti} η^3-methallyl), 1.02 (s, 3H, CH_3 η^3-methallyl). ^{13}C NMR (DMSO-d_6): δ 227.9 (CO), 163.3 (C=O, bipy′), 154.4, 153.2, 145.4, 136.7, 134.5, 125.3, 122.3, 130.1, 121.5 (bipy′), 82.3 (C^2 η^3-methallyl), 53.8 (C^1 and C^3 η^3-methallyl), 21.4 (CH_3, bipy′), 19.6 (CH_3 η^3-methallyl). Anal. Calcd (%) for $C_{32}H_{29}ClMoN_4O_4$: C, 57.80; H, 4.40; N, 8.43. Found: C, 57.67; H, 4.28; N, 8.48.

Synthesis of [MoCl(η^3-methallyl)(CO)$_2$(H$_2$biim)] (4). To a solution of [MoCl(η^3-methallyl)$(CO)_2(NCMe)_2$] (0.250 g, 0.770 mmol) in thf (30 mL) was added H_2biim (0.103 g, 0.770 mmol). The mixture was stirred for 3 h at room temperature. The resulting solution was concentrated under vacuum to a volume of 5 mL, and addition of hexane (10 mL) caused the precipitation of compound **4** as a yellow powder, which was washed with hexane (2 × 20 mL). Yield: 0.265 g, 92%. IR (thf, cm^{-}): 1947, 1852 (ν_{CO}). ^1H NMR (DMSO-d_6): δ 12.63 (br s, 2H, NH, H_2biim), 7.38 (m, 4H, H_2biim), 2.87 (s, 2H, H_{syn} methallyl), 1.14 (s, 2H, H_{anti} η^3-methallyl), 0.97 (s, 3H, CH_3 η^3-methallyl). ^{13}C NMR (DMSO-d_6): δ 227.9 (CO), 139.1, 129.4, 124.0 (H_2biim), 80.0 (C^2 η^3-methallyl), 55.8 (C^1 and C^3 η^3-methallyl), 19.8 (CH_3 η^3-methallyl). Anal. Calcd (%) for $C_{12}H_{13}ClMoN_4O_2$: C, 38.27; H, 3.48; N, 14.87. Found: C, 38.32; H, 3.62; N, 14.69.

Synthesis of [Mo(η^3-methallyl)(CN^{t}Bu)(bipy′)(CO)$_2$]BAr′$_4$ (5). To a solution of [MoCl(η^3-methallyl)$(CO)_2(NCMe)_2$] (0.050 g, 0.153 mmol) in CH_2Cl_2 (20 mL) were added NaBAr′$_4$ (0.136 g, 0.153 mmol) and MeCN (2 mL, excess). The mixture was stirred at room temperature for 5 min, and then, the white solid (NaCl) was filtered off. The solvent was evaporated to dryness, the yellow residue was redissolved in thf (20 mL), bipy′ (0.065 g, 0.153 mmol) was added, and the slurry was stirred at room temperature for 20 min. Then, CN^{t}Bu (0.017 mL, 0.153 mmol) was added and stirred for another 30 min. The solution was concentrated under vacuum to a volume of 5 mL, and addition of hexane (10 mL) caused the precipitation of compound **5** as a black, microcrystalline solid, which was washed with hexane (2 × 20 mL). Yield: 0.183 g, 76%. IR (thf, cm^{-1}): 1965, 1894 (ν_{CO}), 2185 (ν_{CN}). ^1H NMR (DMSO-d_6): δ 10.79 (br s, 2H, NH, bipy′), 9.28 (s, 2H, bipy′), 9.05 (d, J(H,H) = 5.2 Hz, 2H, bipy′), 8.32 (d, J(H,H) = 5.2 Hz, 2H, bipy′), 7.85 (m, 16H, BAr′$_4$ and AA′BB′ of bipy′), 7.62 (m, 4H, H^p BAr′$_4$), 7.11, 7.06 (AA′BB′, 2H, bipy′), 3.65 (s, 2H, H_{syn} methallyl), 2.55 (s, 6H, CH_3 bipy′), 2.15 (s, 2H, H_{anti} η^3-methallyl), 1.12 (s, 9H, CH_3 CN^{t}Bu), 1.01 (s, 3H, CH_3 η^3-methallyl). ^{13}C NMR (DMSO-d_6): δ 225.2 (CO), 165.0 (C=O, bipy′), 163.8 (q, J(C,B) = 49.9 Hz, C^i BAr′$_4$), 156.4, 153.0, 148.1, 138.4, 132.1, 131.9, 125.3, 123.6, 123.5 (bipy′), 136.9 (C^o BAr′$_4$), 129.7 (H_2biim), 131.3 (q, J(C,F) = 31.2 Hz, C^m BAr′$_4$), 126.8 (q, J(C,F) = 271.9 Hz, CF_3 BAr′$_4$), 120.4 (C^p BAr′$_4$), 94.9 (C^2 η^3-methallyl), 69.8 ($C(CH_3)_3$ CN^{t}Bu), 62.2 (C^1 and C^3 η^3-methallyl), 31.8 ($C(CH_3)_3$ CN^{t}Bu), 27.9 (CH_3 η^3-methallyl), 23.3 (CH_3 bipy′), the CN^{t}Bu signal could not be observed. Anal. Calcd (%) for $C_{69}H_{50}BF_{24}MoN_5O_4$: C, 52.59; H, 3.20; N, 4.44. Found: C, 52.69; H, 3.08; N, 4.42.

Synthesis of [Mo(η^3-methallyl)(CN^{t}Bu)(CO)$_2$(H$_2$biim)]BAr′$_4$ (6). To a solution of **4** (0.100 g, 0.266 mmol) in CH_2Cl_2 (30 mL) were added NaBAr′$_4$ (0.236 g, 0.266 mmol) and CN^{t}Bu (0.015 mL, 0.266 mmol). The mixture was stirred at room temperature for 2 h, and then, it was filtered. The solution was concentrated under vacuum to a volume of 5 mL, and addition of hexane (10 mL) caused the precipitation of compound **6** as an orange powder, which was washed with hexane (2 × 20 mL). Yield: 0.300 g, 90%. IR (CH_2Cl_2, cm^{-1}): 1961, 1881 (ν_{CO}), 2185 (ν_{CN}). ^1H NMR (CD_3CN): δ 11.15 (br s, 2H, NH, H_2biim), 7.65 (m, 12H, BAr′$_4$), 7.37 (d, J(H,H) = 1.4 Hz, 2H, H_2biim), 7.22 (d, J(H,H) = 1.4 Hz, 2H, H_2biim), 3.45 (s, 2H, H_{syn} methallyl), 1.96 (s, 2H, H_{anti} η^3-methallyl), 1.20 (s, 9H, CH_3 CN^{t}Bu), 1.08 (s, 3H, CH_3 η^3-methallyl). ^{13}C NMR (CD_3CN): δ 223.8 (CO), 162.5 (q, J(C,B) = 49.9 Hz, C^i BAr′$_4$), 137.9 (H_2biim), 134.6 (C^o BAr′$_4$), 129.7 (H_2biim), 129.1 (q, J(C,F) = 31.0 Hz, C^m BAr′$_4$), 124.5 (q, J(C,F) = 271.9 Hz, CF_3 BAr′$_4$), 120.7 (H_2biim), 117.6 (C^p BAr′$_4$), 89.5 (C^2 η^3-methallyl), 58.4 (C^1 and C^3 η^3-methallyl), 54.3 ($C(CH_3)_3$ CN^{t}Bu), 17.4 (CH_3 η^3-methallyl), the CN^{t}Bu signal could not be observed. Anal. Calcd

---

(23) Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311.

(%) for $C_{49}H_{34}BF_{24}MoN_5O_2$: C, 45.71; H, 2.66; N, 5.44. Found: C, 45.64; H, 2.52; N, 5.63.

Crystal Structure Determination. General Description for Compounds [3]·[NBu_4Cl], [5]·[HSO_4], and [Mo(allyl)(Br/Cl)-($(CO)_2$(H_2Biim)]·[Br/Cl^-]. A suitable crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo Kα X-radiation and a CCD area detector. One hemisphere of the reciprocal space was collected in each case. Raw frame data were integrated with the SAINT[24] program. The structures were solved by direct methods with SHELXTL.[25] An empirical absorption correction was applied with the program SADABS.[26] In every structure, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. In the structure of [Mo(allyl)-(Br/Cl)$(CO)_2$(H_2Biim)], it was found that the positions of Br and Cl were disordered between the two positions (one bonded to Mo, the other hydrogen bonded to the biimidazole ligand). The occupancy of Br and Cl on each site was refined with the constraints EADP and EXYZ, while keeping the total sum to unit for each site. In the structure of [Mo(allyl)(Br/Cl)$(CO)_2$(H_2Biim)], it was found that Br and Cl were disordered between two positions (one bonded to Mo, the other hydrogen bonded to the biimidazole ligand. The occupancy of Br and Cl on each site was refined with the constraints EADP and EXYZ, while keeping the total sum to unit for each site. Despite repeated attempts, it was not possible to find a stable model with different Mo−Cl and Mo−Br distances. Therefore, Cl and Br were refined at the same site, which corresponds to the mean values of the Mo−Cl and Mo−Br distances. Drawings and other calculations were made with SHELXTL, PLATON,[27] and PARST[28] under WINGX.[29] Crystal and refinement details are collected in Table 4.

General Description for Compounds [6]·[Br] and [6]·[ReO_4]. A suitable crystal was mounted directly from the mother liquor under nitrogen at room temperature, perfluorocarbon oil being used to protect it from the atmospheric air and moisture. Data were collected using a Nonius KappaCCD diffractometer. The structures were solved by direct methods, and refinement was carried out using full-matrix least squares on F^2.[30] There is considerable rotational disorder of the ^{t}Bu group, which is especially difficult to model due to the central carbon atom of the ^{t}Bu group lying on a mirror plane. Local maxima within the bonding distance of C9 are included as partial carbon atoms with site occupancies adjusted to give a total of three carbon atoms. The methyl distances on [**6**]·[ReO_4] were constrained to be equal within experimental error. For the structure of [**6**]·[Br], the hydrogen atoms on C5 were directly located, but their thermal parameters were linked to the parent carbon atom. The N(2)−H(2) hydrogen atom was directly located and allowed to refine freely. All other hydrogen atoms in this structure were modeled on idealized geometries and allowed to ride on their parent atoms. For the structure of [**6**]·[ReO_4], the hydrogen atoms on C5 were directly located, but their thermal parameters were linked to the parent carbon atom. All other hydrogen atoms in this structure were modeled on idealized geometries and allowed to ride on their parent atoms. Details of the data collections and structure solutions are given in Table 4.

Acknowledgment. We thank Ministerio de Ciencia y Tecnología (Grants BQU2003-08649 and CTQ2006-07036/BQU) and European Union (ERG to L.R.) for support of this work. L.I. thanks Ministerio de Educación y Ciencia for a FPU predoctoral fellowship. D. Morales and L.R. thank Ministerio de Educación y Ciencia for Ramón y Cajal contracts. R.A.K. would like to acknowledge The States of Guernsey and The Cambridge University Domestic and Millenium Fund.

Supporting Information Available: X-ray crystallographic data for adducts [**3**]·[NBu_4Cl], [**5**]·[HSO_4], [Mo(allyl)(Br/Cl)$(CO)_2$(H_2-Biim)]·[Br/Cl^-], [**6**]·[Br], and [**6**]·[ReO_4] as CIF. ^{1}H NMR titration profiles and Job plot of receptor **5** toward chloride, hydrogensulfate, and nitrate anions. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0621650

---

(24) *SAINT+*, version 6.02; SAX area detector integration program; version 6.02; Bruker AXS, Inc.: Madison, WI, 1999.

(25) Sheldrick, G. M. *SHELXTL*, version 5.1; integrated system for solving, refining, and displaying crystal structures from diffraction data; Bruker AXS, Inc.: Madison, WI, 1998.

(26) Sheldrick, G. M. *SADABS, Empirical Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

(27) (a) For PLATON, see: Spek, A. L. *Acta Crystallogr., Sect A* **1990**, *46*, C34. (b) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 1998.

(28) (a) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95. (b) Nardelli, M. *J. Appl. Crystallogr.* **1995**, *28*, 659.

(29) For WINGX 1.70.00, see: Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(30) Sheldrick, G. M. *SHELX-97*, Göttingen: Göttingen, Germany, 1997.